

Cumulant expansion for fast estimate of non-Condon effects in vibronic transition profiles

Joonsuk Huh^{a,b} and Robert Berger^{a,b*}

^a*Clemens-Schöpf Institute, TU Darmstadt, Petersenstr. 22, 64287 Darmstadt, Germany*

^b*Frankfurt Institute for Advanced Studies, Goethe University,
Ruth-Moufang-Str. 1, 60438 Frankfurt am Main, Germany*

(Dated: November 15, 2011)

When existing, cumulants can provide valuable information about a given distribution and can in principle be used to either fully reconstruct or approximate the parent distribution function. A previously reported cumulant expansion approach for Franck-Condon profiles [Faraday Discuss., 150, 363 (2011)] is extended to describe also the profiles of vibronic transitions that are weakly allowed or forbidden in the Franck-Condon approximation (non-Condon profiles). In the harmonic approximation the cumulants of the vibronic spectral profile can be evaluated analytically and numerically with a coherent state-based generating function that accounts for the Duschinsky effect. As illustration, the one-photon $1^1A_g \rightarrow 1^1B_{2u}$ UV absorption spectrum of benzene in the electric dipole and (linear) Herzberg-Teller approximation is presented herein for zero Kelvin and finite temperatures.

I. INTRODUCTION

Vibrationally resolved electronic spectra (*e.g.* one-photon absorption and emission spectra) are within the Born-Oppenheimer framework usually interpreted in terms of Franck-Condon (FC) factors (FCFs) [1, 2]. Accordingly, one can try to obtain the shape of the spectral profile for a FC-allowed transition from computed FCFs in frequency domain. However, the evaluation of FCFs for large molecular systems is challenging even within the harmonic approximation if one has to take Duschinsky mode mixing (rotation) [3] into account. This is because multi-variate Hermite polynomials have then to be evaluated for each FC integral, rather than only uni-variate Hermite polynomials as is the case for the comparatively simple parallel harmonic oscillator model. The computational task becomes more difficult as the molecular size and temperature increases because the number of FC integrals grows vastly. To describe FC-forbidden or weakly allowed transitions, one has to go beyond the Condon approximation and employ for instance a Herzberg-Teller (HT) expansion [4] of the electronic transition moment with respect to the normal coordinates. As a result, the calculation of the vibronic spectrum for a non-Condon process is even more difficult than for a FC-allowed transition because one has to evaluate many matrix elements of the non-Condon operators which require for each HT integral in general the calculation of combinations of several FC integrals.

The number of FC integrals and matrix elements of non-Condon operators to be evaluated in a sum-over-states approach can be significantly reduced with the help of rigorous integral prescreening strategies [5–7]. However, this time-independent (TI) calculation of the spectral profile in frequency domain is still considerably more

expensive than an alternative time-dependent (TD) approach that exploits time-correlation functions (TCFs) (see *e.g.* Ref. [8]), but offers the ability to directly assign individual peaks in the spectrum. As we have outlined earlier [6, 7, 9], a unified coherent state-based generating function (CSGF) approach [10] can be used both for rigorous integral prescreening strategies and TCF calculations which combine the strengths of both approaches and complement each other favourably. Even in the less demanding TD approach, however, one usually has to invest significant computational time for often unnecessary spectral details.

Cumulants (or moments) of a distribution (see *e.g.* Refs. [10–17]) can deliver highly useful information. From this one can either attempt to reconstruct the spectral shape or try to estimate the relevant spectral profile, which can be exploited in subsequent TI and TD approaches [18]. Cumulants of the vibronic spectrum can be obtained from the CSGF directly without computing the total spectrum in frequency domain. This method was exploited already in Ref. [19] for FC-allowed transitions, and we report herein an extension of this method to incorporate non-Condon transitions. As application, we present the profile of the $1^1A_{1g} \rightarrow 1^1B_{2u}$ transition of benzene, which is in the electric dipole approximation Franck-Condon forbidden, at various temperatures within the linear HT approximation and compare the cumulant expansion result with the TCF approach.

II. METHOD

The spectral profile ($\varrho(\hbar\omega; T)$) can be expressed via the Fourier transform (FT) of the TCF ($\chi(t; T)$) that depends on the time t and temperature T , namely

$$\varrho(\hbar\omega; T) = \hbar^{-1} \int_{-\infty}^{\infty} dt \chi(t; T) e^{i(\omega - \omega_0)t}, \quad (1)$$

* robert.berger@tu-darmstadt.de and huh@fias.uni-frankfurt.de

where $\hbar\omega$ is the transition energy and $\hbar\omega_0$ the $0' - 0$ transition energy. The corresponding occupancy representation for the TCF can be obtained from Fermi's Golden Rule, *i.e.*

$$\chi(t; T) = \frac{\sum_{\underline{v}, \underline{v}'=0}^{\infty} \langle \underline{v}' | \hat{\underline{\mu}}^\dagger(\underline{Q}) | \underline{v} \rangle \langle \underline{v}' | \hat{\underline{\mu}}^*(\underline{Q}) | \underline{v} \rangle^* e^{-iE_{\underline{v}', \underline{\epsilon}} t / \hbar} e^{-\underline{v} \cdot \underline{\epsilon} / (k_B T)}}{\prod_k (1 - e^{-\epsilon_k / (k_B T)})^{-1}}, \quad (2)$$

where we have assumed an electric dipole transition with the electronic transition dipole moment ($\hat{\underline{\mu}}(\underline{Q})$), which is a function of normal coordinates of the initial electronic state. The N -dimensional harmonic oscillator eigenstates of the initial and final electronic state are denoted by $|\underline{v}\rangle$ and $|\underline{v}'\rangle$ with the corresponding harmonic energy vectors $\underline{\epsilon}$ and $\underline{\epsilon}'$, respectively. The vibrational Hamiltonians of the initial and final electronic states are \hat{H} and \hat{H}' , respectively. k_B is the Boltzmann constant. $E_{\underline{v}', \underline{\epsilon}}$ is the vibronic transition energy with respect to the $0' - 0$ transition energy. The time-dependent part with the vibronic transition energy corresponds to a Dirac delta distribution in frequency domain and accordingly this expression is usually evaluated in frequency domain, which is straightforward. The spatial representation of the TCF in closed form can be found by evaluating the following quantum mechanical traces

$$\chi(t; T) = \frac{\text{Tr} \left(\hat{\underline{\mu}}(\underline{Q})^\dagger \exp(-i\hat{H}'t/\hbar) \hat{\underline{\mu}}(\underline{Q}) \exp(i\hat{H}t/\hbar) \exp(-\hat{H}/(k_B T)) \right)}{\text{Tr}(\exp(-\hat{H}/(k_B T)))}. \quad (3)$$

The traces can be evaluated with any complete basis. In our work coherent states were used (see *e.g.* Refs. [5, 7, 9]) with the Duschinsky relation between initial and final state normal coordinates ($\underline{Q}' = \underline{S}\underline{Q} + \underline{d}$ where \underline{S} and \underline{d} are the Duschinsky rotation matrix and displacement vector, respectively and \underline{Q}' are the normal coordinates of the final state) and the HT expansion of the electronic transition dipole moment ($\hat{\underline{\mu}} \simeq \underline{\mu}(\underline{Q}) + \sum_k \underline{\mu}'_k \hat{Q}_k$ where $\underline{\mu}'_k$ is the first derivative of $\underline{\mu}$ with respect to \hat{Q}_k).

The vibronic spectral density function can be related to a probability density function (PDF) because the vibronic transition process follows a certain PDF. If all cumulants or moments of a PDF are defined and available, the PDF can be reconstructed as follows

$$\chi(t, T) = \varrho_{\text{tot}} \exp \left(\sum_{k=1}^{\infty} \frac{\langle E_{\underline{\epsilon}', \underline{\epsilon}}^k \rangle^c(T)}{k!} (it/\hbar)^k \right), \quad (4)$$

where $\langle E_{\underline{\epsilon}', \underline{\epsilon}}^k \rangle^c(T)$ is the k -th order cumulant at temperature T . The cumulants of the spectral density function are normalised to give the total intensity $\varrho_{\text{tot}} = |\underline{\mu}(\underline{Q})|^2 + \sum_k^N \frac{\hbar^2}{2\epsilon_k} |\underline{\mu}'_k|^2 \coth(\frac{\epsilon_k}{2k_B T})$. Moments (cumulants and moments are inter-convertible) can be obtained by partial derivatives of χ with respect to time,

$$\langle E_{\underline{\epsilon}', \underline{\epsilon}}^k \rangle(T) = \left(-\frac{\hbar}{i} \right)^k \frac{\partial^k}{\partial t^k} \chi(t; T) \Big|_{t=0}. \quad (5)$$

Thus, cumulants can be evaluated analytically or numerically by evaluating partial derivatives of χ in Eq. (3) with respect to the time variable at $t = 0$. Analytic evaluation of the cumulants to arbitrary order within the linear HT approximation can be performed along the lines of the development in Refs. [9, 18] for the cumulants of FC profiles to arbitrary order. For numerical evaluation of low-order cumulants one needs to compute χ only at the first few time steps. To obtain the corresponding moments numerically, $\text{Re}(\chi(t, T))$ and $\text{Im}(\chi(t, T))$ are used for the calculation of even and odd moments, respectively, because $e^{-iE_{\underline{\epsilon}', \underline{\epsilon}} t / \hbar} = \cos(E_{\underline{\epsilon}', \underline{\epsilon}} t / \hbar) - i \sin(E_{\underline{\epsilon}', \underline{\epsilon}} t / \hbar)$ in Eq. (2) (see *e.g.* Ref. [16]).

The closed form of $\chi(t, T)$ within the linear HT approximation can be found in Ref. [7, 9]. Therein, additional flexibility was introduced to the GF by distinguishing individual vibrational modes to allow for rigorous pre-screening strategies and detailed control of the dynamics. This can be done by assigning different time and temperature variables to each vibrational degrees of freedom. The corresponding GF in an occupancy representation reads as follows

$$G^K(\underline{z}, \underline{z}'; \underline{B}, \underline{B}')^{(\hat{f}, \hat{g})} = \mathcal{N} |\langle \underline{Q}' | \underline{Q} \rangle|^{-2} \sum_{\underline{v}, \underline{v}'=0}^{\infty} \langle \underline{v}' | \hat{f} | \underline{v} \rangle \langle \underline{v}' | \hat{g} | \underline{v} \rangle^* \prod_{k=1}^N [z_k^{2v_k} (z'_k)^{2v'_k}] e^{-(\underline{v}^\dagger \underline{B} \underline{\epsilon} + \underline{v}'^\dagger \underline{B}' \underline{\epsilon}')}, \quad (6)$$

where the general operators \hat{f} and \hat{g} , which can be products of momentum and position operators, are given instead of $\hat{\underline{\mu}}(\underline{Q})$. The time variables are assigned to the matrices $\underline{z} = \text{diag}(e^{i\epsilon_1 t_1 / (2\hbar)}, \dots, e^{i\epsilon_N t_N / (2\hbar)})$ and $\underline{z}' = \text{diag}(e^{-i\epsilon'_1 t'_1 / (2\hbar)}, \dots, e^{-i\epsilon'_N t'_N / (2\hbar)})$ for initial and final vibrational modes, respectively. Different temperatures can be given to the initial and final vibrational degrees of freedom via $\underline{B} = \text{diag}(1/(k_B T_1), \dots, 1/(k_B T_N))$ and $\underline{B}' = \text{diag}(1/(k_B T'_1), \dots, 1/(k_B T'_N))$, respectively. \mathcal{N} is the corresponding normalising factor.

The electronic $1^1\text{A}_g \rightarrow 1^1\text{B}_{2u}$ transition of benzene is FC-forbidden in the electric dipole approximation ($\underline{\mu}(\underline{Q}) = \underline{0}$) such that only the HT terms contribute to the spectral density function. The corresponding TCF is given as follows, here with same time and temperature (t, T) for all vibrational degrees of freedom,

$$\chi_{\text{FCHT}}(t; T) = |\langle \underline{Q}' | \underline{Q} \rangle|^2 \sum_{i,j} \underline{\mu}'_i \cdot \underline{\mu}'_j G(t; T)^{(\hat{Q}_i, \hat{Q}_j)}. \quad (7)$$

III. RESULTS AND DISCUSSION

The vibronic profiles for benzene's $1^1\text{A}_g \rightarrow 1^1\text{B}_{2u}$ transition at zero Kelvin and finite temperatures are calculated with two methods, namely TCF and time-independent cumulant expansion (CE). We use herein

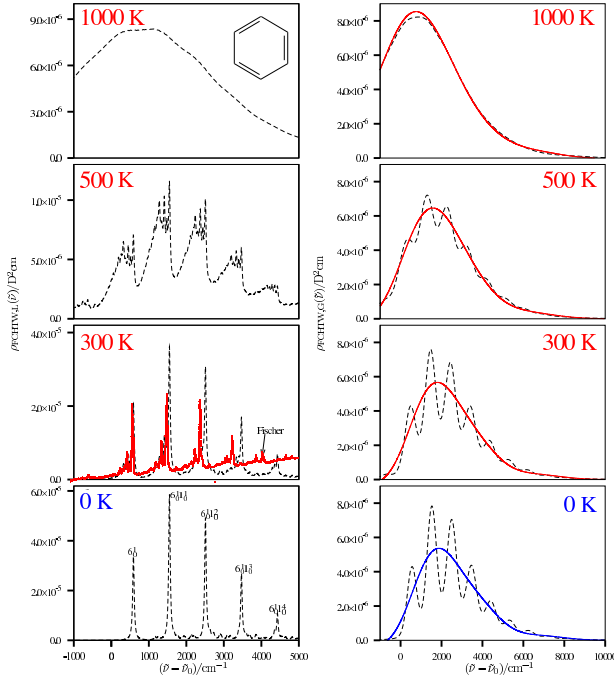


FIG. 1. Left part of the figure: The dashed lines are drawn for the TCF-FFT approach with a Lorentzian line shape function with FWHM of 50 cm^{-1} . A time increment of 0.51 fs and a grid with 2^{16} grid points are used for the corresponding FFT calculations. The experimental UV absorption spectrum of Fischer [20] is additionally shown in red. Right part of the figure: The dashed lines are drawn for the TCF-FFT approach with a Gaussian line shape function of with FWHM of 500 cm^{-1} . A time increment of 0.10 fs and a grid with 2^{15} grid points are used for the corresponding FFT calculations. Solid lines are drawn for the curve obtained by Edgeworth expansion using up to 4-th order cumulants and, for 1000 K by Edgeworth expansion using up to 8-th order cumulants.

the term time-independent CE, which was employed in Ref. [18], to distinguish this CE from the conventional (time-dependent) CE (see *e.g.* Refs. [13–17]) which involves time integration for the cumulant calculation. The spectra obtained are displayed in Fig. 1. To compute the vibronic spectra via the TCF method, the FFTW library [21] is used for fast Fourier Transform (FFT). The approximate curves are generated for the CE with Edgeworth expansion [19, 22] using the computed low-order cumulants. Some of the problems related to this type of expansion for the description of FC profiles are discussed in Ref. [19]. The moments (Eq. 5) are calculated both analytically and numerically, the latter by taking partial derivatives of χ in Eq. 3 with respect to time. Analytical and numerical results are compared in Table I. Required input data from electronic structure calculations for benzene, *i.e.* molecular equilibrium structures and corresponding harmonic force fields for each electronic state (1A_g and $^1B_{2u}$) as well as first derivatives of the electronic transition dipole moments are taken from Ref. [23]

(CASSCF/DZV). These data have recently been compared to results obtained via analytical derivatives techniques for electronic transition dipole moments within a time-dependent density functional theory framework [24]. The vibronic structure methods employed in the present work are implemented in a development version of our vibronic structure program package hotFCHT [5–7, 18, 23].

The left hand side in Fig. 1 shows vibronic profiles from TCF-FFT which are convoluted by a Lorentzian line shape function with full width at half maximum (FWHM) of 50 cm^{-1} at temperatures elevating from 0 K to 1000 K . This FC-forbidden vibronic transition is mediated by the non-totally symmetric vibrational modes in the irreducible representation e_{2g} . The main feature of the vibronic spectrum is from progressions in the totally symmetric C-C stretching mode (963 cm^{-1}) building on the so-called false origin from a single excitation of a non-totally symmetric (e_{2g}) in-plane bending mode (575 cm^{-1}) as indicated in the spectrum at zero Kelvin. The calculated spectrum at 300 K is compared with the experimental data of Fischer [20]. The two spectra agree fairly well in the low energy region but the computed peaks at higher energies are slightly shifted to larger wavenumbers due to the harmonic approximation. As temperature increases the vibrational structure becomes very congested and washed out. At 1000 K (only employed for testing the method) one can not see a resolved vibrational structure any longer, only the corresponding envelope.

On the right hand side of Fig. 1 the two methods (TCF-FFT and CE-Edgeworth) are compared for increasing temperatures. The spectra are convoluted in the TCF-FFT curves (dashed lines) with a Gaussian line shape function of 500 cm^{-1} for FWHM. The second moments ($4.51 \times 10^4 \text{ cm}^{-2} (hc_0)^2$) of the Gaussian line shape function is added to the second moments of the vibronic spectrum to take the line shape function into account (see Ref. [19] for the rationalisation and details). The relatively broad line shape function is used for the TCF-FFT curves to have vibrationally relatively structureless spectra for comparison. At $0, 300$ and 500 K , the TCF-FFT curves still show vibrational structure and the CE-Edgeworth curves (solid lines) look like non-linear regression curves of the corresponding TCF-FFT spectra. When the vibrational structures are also essentially smoothed out in the TCF-FFT curves at 1000 K , the two approaches agree with each other extremely well. Up to the 4-th order cumulants are used for $0, 300, 500 \text{ K}$ and up to 8-th order cumulants are computed for 1000 K .

In table I the moments computed numerically (via derivatives) and analytical are compared. At low orders and all temperatures the two methods agree well and for higher orders still the agreement is satisfactory. One of the advantages of the numerical method is that one only needs to compute the TCF for the first few time steps. The analytical method usually meets a combinatorial problem in high order cumulant calculations due to the analytic derivatives of the inverse matrix. The second

advantage is that it is easy to include linear and nonlinear non-Condon effects. The third advantage is that one can incorporate general line shape functions which would not have well defined cumulants (see the discussion on page 415 of Ref. [25]).

TABLE I. Analytically and numerically computed cumulants. $4.51 \times 10^4 \text{ cm}^{-2} (hc_0)^2$ is added to the second moments to take the Gaussian line shape function (FWHM = 500 cm^{-1}) into account; see Ref. [19] for details. A time increment of 0.10 fs is used for computing the numerical derivatives.

n	$\langle E_{\text{ex}}^n \rangle / (\text{cm}^{-1} hc_0)^n$							
	$T = 0 \text{ K}$		$T = 300 \text{ K}$		$T = 500 \text{ K}$		$T = 1000 \text{ K}$	
	Analytical	Numerical	Analytical	Numerical	Analytical	Numerical	Analytical	Numerical
1	2.61×10^3	2.61×10^3	2.47×10^3	2.47×10^3	2.12×10^3	2.12×10^3	1.12×10^3	1.12×10^3
2	9.24×10^6	9.21×10^6	8.64×10^6	8.62×10^6	7.38×10^6	7.36×10^6	5.64×10^6	5.63×10^6
3	4.07×10^{10}	4.05×10^{10}	3.77×10^{10}	3.75×10^{10}	3.17×10^{10}	3.15×10^{10}	2.03×10^{10}	2.01×10^{10}
4	2.14×10^{14}	2.12×10^{14}	1.97×10^{14}	1.95×10^{14}	1.66×10^{14}	1.64×10^{14}	1.29×10^{14}	1.27×10^{14}
5	-	-	-	-	-	-	8.00×10^{17}	7.82×10^{17}
6	-	-	-	-	-	-	6.55×10^{21}	6.33×10^{21}
7	-	-	-	-	-	-	5.84×10^{25}	5.54×10^{25}
8	-	-	-	-	-	-	6.16×10^{29}	5.71×10^{29}

TABLE II. Mean excitation wavenumbers of individual vibrational modes in e_{2g}

Mode (cm^{-1})	0 K (cm^{-1})	300 K (cm^{-1})	500 K (cm^{-1})	1000 K (cm^{-1})
575	2.62×10^2	2.90×10^2	3.79×10^2	7.25×10^2
575	2.62×10^2	2.90×10^2	3.79×10^2	7.25×10^2
1237	1.60×10^1	1.78×10^1	4.64×10^1	2.51×10^2
1237	1.60×10^1	1.78×10^1	4.64×10^1	2.51×10^2
1665	2.54×10^1	2.38×10^1	3.09×10^1	1.65×10^2
1665	2.54×10^1	2.38×10^1	3.09×10^1	1.65×10^2
3389	8.14×10^1	7.49×10^1	6.08×10^1	6.37×10^1
3389	8.14×10^1	7.49×10^1	6.08×10^1	6.37×10^1

Mean excitation wavenumbers are computed for the HT active e_{2g} symmetric vibrational modes of the final state. The mean excitation energy can serve as a parameter for the individual vibrational degrees of freedom as an effective reorganisation energy or a Huang-Rhys factor (when normalised by its harmonic energy), which can be characterised as a function of structural deformation, frequency change, Duschinsky mode coupling and temperature both in the Condon and non-Condon approximation. One might naively expect a larger mean excitation energy as the temperature increases but the mean values of high frequency modes (1665 and 3389 cm^{-1}) in some intermediate temperature ranges are smaller than at zero Kelvin. This can be rationalised as follows: Because the Duschinsky mode mixing between low and high frequency modes is small in the present case, the high frequency modes can not obtain thermal energy from the low frequency modes efficiently. Thus the high frequency modes are almost thermally inactive, whereas the total intensity (ρ_{tot}) in-

creases as temperature increases. In the mean energy calculation of the high frequency modes at finite temperatures the denominator (total intensity) increases because low frequency modes accept thermal energy while the numerator (excitation of high frequency modes) stays constant. Therefore the mean excitation energies of high frequency modes are reduced at finite temperatures. If Duschinsky rotation couples the low and high frequency modes significantly (see *e.g.* Ref. [26]), however, thermal energy can be transferred to the high frequency modes via the low frequency modes in the initial state, accordingly the mean excitation energies of high frequency modes can increase as temperature increases.

IV. CONCLUSION AND OUTLOOK

We have discussed a cumulant expansion method for describing non-Condon transitions and applied it to the prototypical one-photon electric dipole $1^1A_g \rightarrow 1^1B_{2u}$ transition of benzene, which is FC forbidden but HT allowed in the linear HT approximation. The method is particularly powerful when one does not require all the details of the vibronic structures, but rather only quantities such as peak maximum, mean and variance of the spectral shape. This method is computationally much cheaper than the sum-over-states and time-correlation function approach. Moreover, the information (*e.g.* relevant energy window) from the cumulant expansion method can be used in the calculation within the other two methods. Herein we compared a numerical approach for the calculation of cumulants with the results from an analytical scheme. The results obtained numerically are still fairly good. With this method, one can incorporate easily nonlinear non-Condon terms and various line shape functions. In the time-correlation function calculation the real part and imaginary part at each time step provide automatically the even and odd moments, respectively. In the first few time steps we already have the first few moments available and the probability distribution function (information) becomes complete as time progresses.

ACKNOWLEDGEMENTS

Financial support by the Beilstein-Institut, Frankfurt/Main, and computer time provided by the Center for Scientific Computing (CSC) Frankfurt are gratefully acknowledged. We are indebted to Jason Stuber for discussions.

-
- [1] J. Franck, Trans. Faraday Soc. **21**, 536 (1925).
 - [2] E. U. Condon, Phys. Rev. **32**, 858 (1928).
 - [3] F. Duschinsky, Acta Physicochim. URSS **7**, 551 (1937).

- [4] G. Herzberg and E. Teller, Z. Phys. Chem. B **21**, 410 (1933).

- [5] H.-C. Jankowiak, J. L. Stuber, and R. Berger, *J. Chem. Phys.* **127**, 234101 (2007).
- [6] J. Huh, H.-C. Jankowiak, J. L. Stuber, and R. Berger, (to be published).
- [7] J. Huh, J. L. Stuber, and R. Berger, (to be published).
- [8] D. J. Tannor and E. J. Heller, *J. Chem. Phys.* **77**, 202 (1982).
- [9] J. Huh, Dissertation (2010).
- [10] E. V. Doktorov, I. A. Malkin, and V. I. Man'ko, *J. Mol. Spectrosc.* **77**, 178 (1979).
- [11] L. S. Cederbaum and W. Domcke, *Adv. Chem. Phys.* **36**, 205 (1977).
- [12] E. J. Heller, *J. Chem. Phys.* **68**, 2066 (1978).
- [13] R. Islampour, *Chem. Phys.* **133**, 425 (1989).
- [14] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995).
- [15] H. Wadi and E. Pollak, *J. Chem. Phys.* **110**, 11890 (1999).
- [16] G. C. Schatz and M. A. Ratner, *Quantum mechanics in chemistry* (Dover Publications, Inc., New York, 2002).
- [17] K. K. Liang, A. M. Mebel, S. H. Lin, M. Hayashi, H. L. Selzle, E. W. Schlag, and M. Tachiya, *Phys. Chem. Chem. Phys.* **5**, 4656 (2003).
- [18] J. Huh, J. L. Stuber, and R. Berger, (to be published).
- [19] J. Huh and R. Berger, *Faraday Discuss.* **150** (2011).
- [20] G. Fischer, *Vibronic Coupling* (Academic Press Inc., London, 1984).
- [21] M. Frigo and S. G. Johnson, *Proceedings of the IEEE* **93**, 216 (2005), special issue on "Program Generation, Optimization, and Platform Adaptation".
- [22] S. Blinnikov and R. Moessner, *Astron. Astrophys. Suppl. Ser.* **130**, 193 (1998).
- [23] R. Berger, C. Fischer, and M. Klessinger, *J. Phys. Chem. A* **102**, 7157 (1998).
- [24] S. Coriani, T. Kjærgaard, P. Jørgensen, K. Ruud, J. Huh, and R. Berger, *J. Chem. Theory Comp.* **6**, 1028 (2010).
- [25] *Faraday Discuss.* **150** (2011).
- [26] J. Huh, P. O. J. Scherer, S. F. Fischer, and R. Berger, (to be published).